CHINA PARTICUOLOGY Vol. 3, No. 5, 265–270, 2005

DENSITY FUNCTIONAL FOR STRUCTURES OF COLLOIDS CONFINED IN A SLIT-LIKE PORE

Fengqi You, Sheng Fu, Yangxin Yu* and Guanghua Gao

State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, P. R. China
**Author to whom correspondence should be addressed. E-mail: yangxyu@mail.tsinghua.edu.cn*

Abstract A density functional theory is applied to calculating the local density profiles of colloids confined in a slit-like pore as well as the radial distribution functions of bulk colloids. The interaction between the colloidal particles is described using a hard-core Yukawa model. The excess Helmholtz energy functional is a combination of the modified fundamental measure theory of Yu and Wu (2002) for the hard-core contribution and a corrected mean-field theory for the attractive contribution. Comparison with the results from the Monte Carlo simulations shows that the corrected theory improves the density profiles of colloids in the vicinity of contact over the original mean-field theory. Both the present corrected theory and simulations suggest that there are depletion and desorption for the colloid with strong attraction between particles at low temperature.

Keywords colloid, slit-like pore, inhomogeneous fluid, fundamental theory, Yukawa model

1. Introduction — A Review on Methodology and Our Strategy

Recently, close-packed monodisperse silica or latex nanoparticles have been proposed for application in microphotonic crystal devices and chips (Yang et al., 2002). Understanding the fundamental mechanisms that drive the assembly of particles at microscopic level will bring about new strategies for the fabrication of well-ordered arrays of nanoscale objects. On the other hand, the structure of colloids in a confined geometry is closely related to this self-assembly of colloidal particles for material applications. Since the interaction between the colloidal particles is well described by the hard-core Yukawa (HCY) potential (Gonzalez-Mozuelos et al., 1991), investigation on the static density distribution of the HCY fluids would provide a useful starting point for understanding the self-assembly of colloidal particles and the microscopic flow behavior.

A lot of researches have been carried out to investigate the pair correlation functions, phase equilibria, thermodynamic properties and surface tensions of the pure HCY fluids using integral equation theory, perturbation theory and Monte Carlo simulations (Gonzalez-Mozuelos et al., 1991; Sese & Bailey, 2003; Cochran & Chiew, 2004; Shukla, 2000; Duh & Mier-y-Teran, 1997; Henderson et al. 1995), while few have been done for the HCY fluid mixtures (Vazquez et al., 2003). As for the inhomogeneous HCY fluids, all studies were limited to one-component attractive and repulsive HCY fluids. For example, Olivares-Rivas et al. (1997) used the singlet hypernetted chain integral equation and a modified version of the Lovett-Mou-Buff-Wertheim equation to predict the density profiles near a hard wall at reduced density $\rho_b\sigma^3 = 0.7$. Several versions (Yi & Kim, 1997; Tang & Wu, 2004; Tang, 2004; You et al., 2005) of density functional theory (DFT) have also been developed for the pure HCY fluid confined in a pore or near a wall.

In our previous work (You et al., 2005), we applied the grand canonical ensemble Monte Carlo (GCMC) simulation and the DFT to investigating the structures of attractive and repulsive HCY fluids near a wall as well as the radial distribution functions of the bulk HCY fluids, and an excellent agreement between theory and simulation is obtained. In this work, we continue our investigation on inhomogeneous colloids using the HCY potential. The key problem of a DFT is that we have to find a good approximation for the excess Helmholtz energy functional. DFT has enjoyed some remarkable successes for hard-sphere fluids. In particular, the modified fundamental measure theory (MFMT) yields very accurate density profiles for inhomogeneous hard-sphere fluids (Yu & Wu, 2002; Pizio et al. 2004) and is easy to apply to multicomponent and polydisperse hard-sphere fluids (Yu et al., 2004). In contrast, DFTs for the dispersion force are satisfactory only in the case of one-component systems. A convenient way is to use the popular mean-field (MF) theory (Gu et al., 2003; Zhang et al., 2003), which is simple, computationally efficient and can be applied to multicomponent systems directly. The shortcoming of the MF theory is apparent: it neglects the fluid structure completely, and its performance is highly system-dependent (Wilemski & Li, 2004). It usually overestimates the density at a hard surface, and gives too strong oscillations of density profiles (Tang, 2004; You et al., 2005). It is reduced to the well-known van der Waals equation of state at the homogeneous limit. Some modifications (Lu et al., 1985; Velasco & Tarazona, 1989) have been made to improve the MF theory, but they are semi-empirical and do not solve the fundamental problems in the MF theory. A recent modification (Katsov & Weeks, 2001; 2002) of the MF theory adopts the so-called effective reference field and has successfully addressed the interfacial and hydrophobic phenomena in inhomogeneous fluids (Huang & Chandler, 2002). In this work, the Helmholtz energy functional of the HCY fluid is constructed by

combining the MFMT for the hard-core interaction with the MF theory for the Yukawa dispersion interaction. To overcome the shortcoming of the MF theory, we introduce a constant *c* to "correct" the MF theory just as we correct the energy parameter *a* in the well-known van der Waals equation of state. The constant *c* is determined from the bulk chemical potentials of pure HCY fluids. And then, the theory is applied to investigating the density profiles and radial distribution functions of colloids represented by the hard-core Yukawa potential.

In what follows, we present the DFT theory for a HCY fluid in Section II, the numerical results for the density profiles and the radial distribution functions in Section III, and a few general conclusions in Section IV.

2. Theory

2.1 Model

We consider colloidal particles interacting via the pairwise-additive two-body potential given by

$$u(r)=\begin{cases}\infty & r<\sigma\\ -\dfrac{\varepsilon\sigma\exp[-\lambda(r-\sigma)/\sigma]}{r} & r>\sigma\end{cases}, \tag{1}$$

where σ is the hard-core diameter, ε is the energy parameter, r is the center-to-center distance between two interacting Yukawa spheres, and λ is a screening length for the Yukawa tail. Throughout this work, the hard-sphere Yukawa potential with the range parameter $\lambda=1.8$ is used. In this work we investigate the structures of colloids confined in a slit-like pore under different conditions using the density functional theory.

2.2 Density functional theory

The essential task for a density functional theory is to derive an analytical expression for the grand potential Ω, or equivalently, the intrinsic Helmholtz free energy F, as a functional of density distribution $\rho(\mathbf{r})$. For a HCY fluid at given temperature T, total volume V, chemical potential μ, and external potential $V^{\text{ext}}(\mathbf{r})$, the grand potential is minimized at equilibrium and the equilibrium density distribution $\rho(\mathbf{r})$ satisfies

$$\delta\Omega[\rho(\mathbf{r})]/\delta\rho(\mathbf{r}')=0\,. \tag{2}$$

The grand potential for an inhomogeneous HCY fluid is related to the Helmholtz energy functional through the Legendre transform

$$\Omega[\rho(\mathbf{r})]=F[\rho(\mathbf{r})]+\int d\mathbf{r}\rho(\mathbf{r})[V^{\text{ext}}(\mathbf{r})-\mu]\,. \tag{3}$$

Once we have an expression for the intrinsic Helmholtz free energy, the solution to Eq. (2) gives the equilibrium density profiles and subsequently, relevant thermodynamic properties.

To take into account the non-ideality arising from inter-molecular interactions, the intrinsic Helmholtz free energy functional is often expressed as contributions from an ideal gas term and an excess term due to intermolecular interactions

$$F=F^{\text{id}}+F^{\text{ex}}\,, \tag{4}$$

where the ideal intrinsic Helmholtz energy functional F^{id} is known exactly,

$$F^{\text{id}}=k_{\text{B}}T\int d\mathbf{r}\left[\ln(\rho(\mathbf{r})\Lambda^3)-1\right]\rho(\mathbf{r})\,, \tag{5}$$

where k_{B} is the Boltzmann constant, T is the absolute temperature, and $\Lambda=h/(2\pi mk_{\text{B}}T)^{1/2}$ is the thermal de Broglie wave length.

The central topic of a density functional theory is to derive an analytical expression for the excess Helmholtz free energy as a functional of the density distributions. The excess Helmholtz free energy functional can be further decomposed into the contributions from the hard sphere repulsion and long-ranged attraction:

$$F^{\text{ex}}=F^{\text{ex}}_{\text{hs}}+F^{\text{ex}}_{\text{att}}\,. \tag{6}$$

As in the previous work (You et al., 2005), we apply the MFMT (Yu & Wu, 2002; Yu et al., 2004) for the functional $F^{\text{ex}}_{\text{hs}}$ in Eq. (6). The mathematical expression of the MFMT excess Helmholtz free energy functional is given by

$$F^{\text{ex}}_{\text{hs}}=k_{\text{B}}T\int\Phi^{\text{hs}}[n_\alpha(\mathbf{r})]d\mathbf{r}\,, \tag{7}$$

where $\Phi^{\text{hs}}[n_\alpha(\mathbf{r})]$ is the reduced excess Helmholtz free energy density due to hard-sphere repulsion, and $n_\alpha(\mathbf{r})$ is the weighted density, which can be expressed as

$$n_\alpha(\mathbf{r})=\int d\mathbf{r}'\rho(\mathbf{r}')w^{(\alpha)}(|\mathbf{r}-\mathbf{r}'|)\,, \tag{8}$$

where the subscripts $\alpha=0, 1, 2, 3, V1$ and $V2$ denote the index of six weight functions $w^{(\alpha)}(r)$, which can be found in our previous work (Yu & Wu, 2002; 2003) and the paper of Rosenfeld (1989). In the MFMT, the Helmholtz free energy density due to hard sphere repulsion consists of contributions from the scalar-weighted densities and the vector-weighted densities (Yu & Wu, 2002; Yu et al., 2004):

$$\Phi^{\text{hs}}[n_\alpha(\mathbf{r})]=\Phi^{\text{hs}(S)}[n_\alpha(\mathbf{r})]+\Phi^{\text{hs}(\boldsymbol{V})}[n_\alpha(\mathbf{r})]\,, \tag{9}$$

where the superscripts (S) and (***V***) stand for the contributions from the scalar and vector weighted densities, respectively. The scalar Helmholtz energy density is given by

$$\Phi^{\text{hs}(S)}[n_\alpha(\mathbf{r})]=$$

$$-n_0\ln(1-n_3)+\frac{n_1n_2}{1-n_3}+\frac{n_2^3\ln(1-n_3)}{36\pi n_3^2}+\frac{n_2^3}{36\pi n_3(1-n_3)^2}\,, \tag{10}$$

and the vector part is expressed by

$$\Phi^{\text{hs}(\boldsymbol{V})}[n_\alpha(\mathbf{r})]=-\frac{\mathbf{n}_{V1}\bullet\mathbf{n}_{V2}}{1-n_3}-\frac{n_2\mathbf{n}_{V2}\bullet\mathbf{n}_{V2}\ln(1-n_3)}{12\pi n_3^2}-\frac{n_2\mathbf{n}_{V2}\bullet\mathbf{n}_{V2}}{12\pi n_3(1-n_3)^2}\,. \tag{11}$$

In the limit of a bulk fluid, the two vector weighted densities $\mathbf{n}_{V1}$ and $\mathbf{n}_{V2}$ vanish, and the Helmholtz free energy density Φ^{hs} becomes identical to that from the Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) equation of state (Boublik, 1970; Mansoori et al., 1971).

The attractive part of the Helmholtz energy functional can be expressed as

$$F_{\text{att}}^{\text{ex}}\left[\rho(\mathbf{r})\right]=\frac{1}{2}\iint \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r}')g(\mathbf{r},\mathbf{r}')u(|\mathbf{r}-\mathbf{r}'|), \quad (12)$$

where $g(\mathbf{r},\mathbf{r}')$, the radial distribution function (RDF) between spheres for the inhomogeneous fluid, is generally difficult to obtain. But if we set $g(\mathbf{r},\mathbf{r}')=1$, the above equation is reduced to the most popular form for the dispersion force — the mean-field (MF) theory:

$$F_{\text{att}}^{\text{ex}}\left[\rho(\mathbf{r})\right]=\frac{1}{2}\iint \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r}')u(|\mathbf{r}-\mathbf{r}'|). \quad (13)$$

Apart from its simplicity in form and its computational efficiency, the MF theory often overestimates the contact values of density and the oscillations of density profiles due to its complete neglect of the fluid structure. In this work, we introduce a constant *c* to "correct" the attractive part of excess Helmholtz energy functional, where *c* is related to the fluid properties just as the correction to the parameter *a* in the well-known van der Waals equation of state. From the comparison between the simulation results of chemical potential for pure hard-core Yukawa fluid, and the hard sphere part of chemical potential from the BMCSL equation of state (Boublik, 1970; Mansoori et al., 1971), we can obtain the value of parameter *c* under different conditions. Thus the attractive part of Helmholtz free energy functional is expressed as

$$F_{\text{att}}^{\text{ex}}\left[\rho(\mathbf{r})\right]=\frac{c}{2}\iint \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r}')u(|\mathbf{r}-\mathbf{r}'|). \quad (14)$$

At equilibrium, the grand potential $\Omega[\rho(\mathbf{r})]$ reaches its minimum. From Eq. (2), we can obtain the following Euler-Lagrange equation for the density profile:

$$\rho(\mathbf{r})=\rho_{\text{b}}\exp\left\{\beta\mu^{\text{ex}}-\int \mathrm{d}\mathbf{r}'\left[\sum_{\alpha}\frac{\partial\Phi^{\text{hs}}}{\partial n_{\alpha}(\mathbf{r})}w^{(\alpha)}(|\mathbf{r}'-\mathbf{r}|)\right]-\right.$$

$$\left.\beta V^{\text{ext}}(\mathbf{r})-c\beta\int \mathrm{d}\mathbf{r}'\rho(\mathbf{r}')u(|\mathbf{r}-\mathbf{r}'|)\right\}, \quad (15)$$

where $\beta=1/k_{\text{B}}T$, $F_{\text{hs}}^{\text{ex}}$ is evaluated from Eq. (7), ρ_{b} is the bulk density and μ^{ex} is the excess chemical potential, i.e.,

$$\mu^{\text{ex}}=\mu_{\text{hs}}^{\text{ex}}+c\mu_{\text{MF}}^{\text{ex}}, \quad (16)$$

where $\mu_{\text{hs}}^{\text{ex}}$ is the excess chemical potential due to hard sphere repulsion, which can be obtained from the BMCSL equation of state (Boublik, 1970; Mansoori et al., 1971), and $\mu_{\text{MF}}^{\text{ex}}$ is obtained by the functional derivative of Eq. (13) with respect to the density distribution in the bulk limit. Let us call this density functional theory as MFMT-cMF theory, and note that when $c=1$, it reduces to the mean-field (MFMT-MF) theory.

When colloids are confined in a slit-like pore, the density profiles vary only in the *z*-direction, i.e., $\rho(\mathbf{r})=\rho(z)$. The density profiles are solved from Eq. (15) using the Picard-type iterative method. In the calculation, iteration starts with the corresponding bulk density as an initial guess. The next input is obtained by mixing the new density profile with the previous one. The numerical integrations are performed using the trapezoidal rule with the step size Δz, or $\Delta r=0.005\sigma$, and the iteration repeats until the percentage change is smaller than 10^{-4} at all points.

3. Results and Discussion

3.1 Colloids in a slit-like pore

To obtain density profiles from Eq. (15), we need to determine the constant *c* first. We simulate the excess chemical potential by the Widom test particle method for the pure HCY fluid with $\lambda=1.8$ at different temperatures and reduced densities. We also find that parameter *c* is independent of temperature and varies linearly with density. For convenience, we use $c=1+0.56\rho_{\text{b}}\sigma^3$ at all densities and temperatures throughout this work.

Now let us discuss the density profiles of the colloids in a slit-like pore under various conditions. The external potential from the parallel walls can be expressed as

$$V^{\text{ext}}(z)=\begin{cases}W(z)+W(H-z) & \sigma/2\le z\le H-\sigma/2\\ \infty & \text{otherwise}\end{cases}, \quad (17)$$

where

$$W(z)=-\varepsilon_{\text{W}}\exp\{-\lambda(z-\sigma/2)/\sigma\}, \quad (18)$$

where ε_{W} is the energy parameter of the wall, H is the width of the slit-like pore and z is the perpendicular distance from the left wall. The bulk conditions used in the calculations are specified by the reduced temperature $T^*=k_{\text{B}}T/\varepsilon$, and the bulk reduced density $\rho^*=\rho_{\text{b}}\sigma^3$. In all the calculations in this work, σ is selected as the unit length and the pore width $H=10\sigma$.

In Fig. 1, we compare the calculated density profiles in a slit-like pore ($H=10\sigma$) with that from the grand canonical ensemble Monte Carlo (GCMC) simulations for the colloidal particles at reduced temperature $T^*=2.0$ and reduced densities $\rho_{\text{b}}\sigma^3=0.4$ and 0.7, respectively. In all the cases for the colloids confined in the slit-like pore, two wall parameters $\varepsilon_{\text{W}}/k_{\text{B}}T=0$ and 1.0 are considered. From Fig. 1(a) one can see that the density profiles exhibit less oscillation near a hard wall at low bulk density. When the wall has an attractive force, there is an accumulation of the colloids near the wall. The MFMT-cMF theory accurately predicts the density profiles near the wall, while the MFMT-MF theory slightly overestimates the density in the vicinity of the wall at low bulk density. As the bulk density is increased, the oscillation of the density profiles becomes more pronounced, as can be seen from Fig. 1(b)

In Fig. 2, the density profiles predicted from the

MFMT-cMF and MFMT-MF theories are compared with those from the GCMC simulations at reduced density $\rho_b\sigma^3 = 0.7$ and reduced temperatures T^*=1.25 and 1.1, respectively. At these two states, the attractive hard-core Yukawa fluid is near the vapor-liquid transition temperature. When $\varepsilon_W = 0$, the density profiles have fewer oscillations and approach monotonically to the wall. The depletion of attractive hard-core Yukawa fluids near a wall at low temperature ($T^* = 1.1$) is the result of the competition between excluded-volume and attractive interaction: the former favors accumulation of colloids near the wall, while the latter restricts the colloids from approaching the wall. At low temperature, the attractive interaction prevails and the density profile shows depletion. Comparison with the GCMC simulation data suggests that the density profiles predicted from the MFMT-cMF theory are very accurate. In contrast, the MFMT-MF theory overestimates the density at contact and gives incorrect oscillatory behaviors, as can be seen in Fig. 2(b). The MFMT-MF theory is not only quantitatively unreliable but also qualitatively questionable due to its failure to describe the depletion near the wall at low temperature.

From Figs. 1 and 2 we can conclude that at high temperatures or for the attractive walls, the density profiles of attractive hard-core Yukawa fluid oscillate with a periodicity of a hard-sphere diameter σ. The higher the wall energy parameter ε_W is, the larger the magnitude of density oscillation. The density profiles shift toward the wall as density is increased and there is a significant accumulation of colloids near the wall at high density and large value of ε_W. The results predicted from the MFMT-cMF theory are in good agreement with that from the GCMC simulations, while the MFMT-MF theory overestimates the density at contact and fails to explain the depletion near the hard wall at low temperature. The disadvantages of the MF theory are caused by its too high chemical potentials, and the MFMT-cMF theory overcomes this shortcoming.

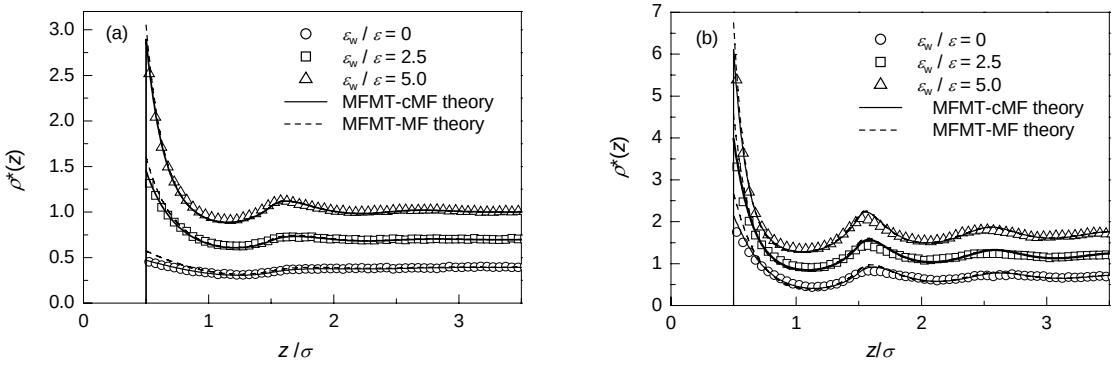

Fig. 1 Reduced density profiles for an attractive Yukawa fluid in a slit-like pore at reduced densities $\rho_b\sigma^3 = 0.4$ ((a), on the left) and $\rho_b\sigma^3 = 0.7$ ((b), on the right) and reduced temperature $T^* = 2.0$. The symbols, solid and dashed curves represent the results from the grand canonical ensemble Monte Carlo (GCMC) simulation, MFMT-cMF and MFMT-MF theories, respectively. To enhance visual clarity, the profiles for $\varepsilon_W/\varepsilon = 2.5$ and 5.0 are shifted upward by 0.3 and 0.6, respectively ((a), on the left), and by 0.5 and 1.0, respectively ((b), on the right).

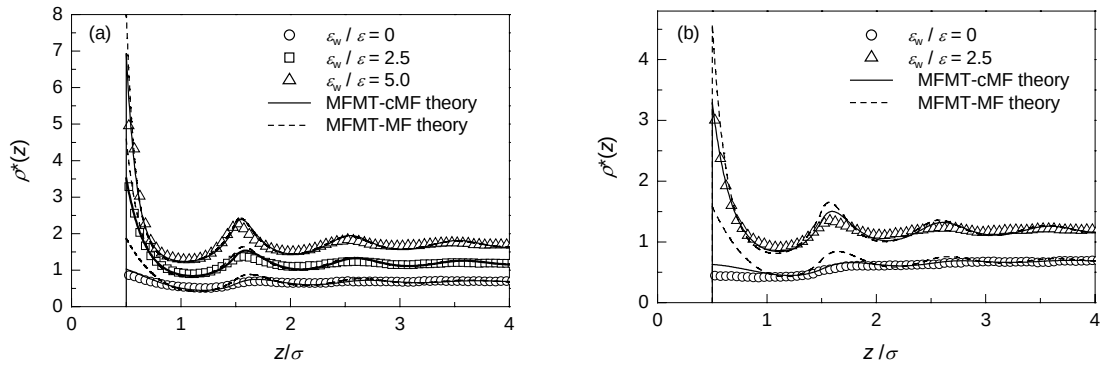

Fig. 2 Reduced density profiles for an attractive Yukawa fluid in a slit-like pore at reduced density $\rho_b\sigma^3 = 0.7$ and reduced temperature T^*=1.25 ((a), on the left) and $T^* = 1.1$ ((b), on the right). The symbols, dashed and solid curves represent the results from the GCMC simulation, MFMT-MF and MFMT-cMF theories, respectively. To enhance visual clarity, the profiles of $\varepsilon_W/\varepsilon = 2.5$ and 5.0 are shifted upward by 0.5 and 1.0, respectively.

3.2 Radial distribution function of colloidal particle

Based on the idea of Percus' test-particle method, the DFT can be used to calculate the radial distribution functions of the bulk colloidal particles represented by the HCY potential. For a colloidal particle fixed in space, the external potential it produces is given by

$$V^{\text{ext}}(r)=\begin{cases}\infty & r<\sigma\\ -\dfrac{\varepsilon\sigma\exp[-\lambda(r/\sigma-1)]}{r} & r\geq\sigma\end{cases}. \tag{19}$$

If the density profile of other spheres around the fixed particle is calculated from the DFT, the radial distribution function $g(r)$ can be obtained through

$$g(r)=\rho(r)/\rho_{\text{b}}. \tag{20}$$

Eq. (20) has been applied to pure HCY fluid. Figure 3(a) depicts the predicted radial distribution functions for colloids represented by the attractive hard-core Yukawa fluids at reduced temperature $T^*=2.0$, and reduced densities $\rho_{\text{b}}\sigma^3=0.3$ and 0.8, along with the Monte Carlo data of Shukla (2000). The agreement between the present MFMT-cMF theory and the computer simulation is excellent. However, as the temperature is decreased (see Fig. 3(b)), the present MFMT-cMF theory overestimates the radial distribution function at contact and gives too strong oscillations. Because at low temperature the attractive force between colloidal particles becomes dominant, we can conclude that the hard-core contributions to the Helmholtz free energy functional in the present MFMT-cMF theory is accurate and the deviations from the MC simulation are produced by the mean field part. Further work is needed to accurately describe the attractive part of the Helmholtz free energy functional.

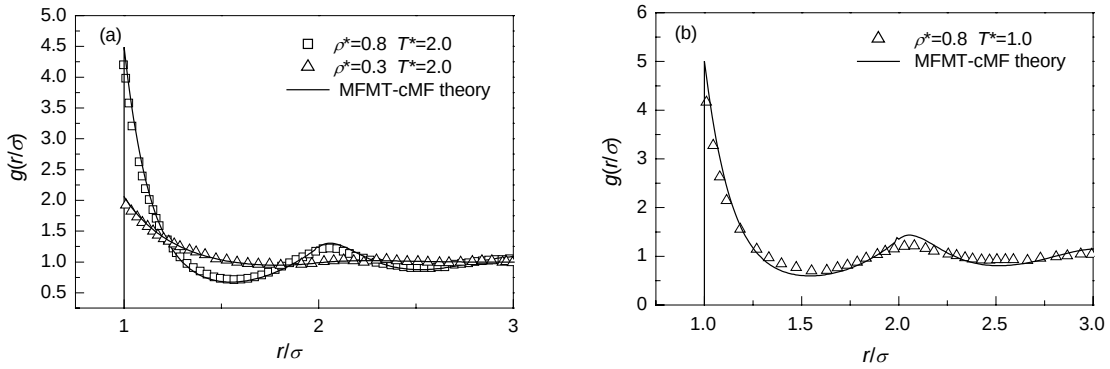

Fig. 3 Radial distribution functions of attractive Yukawa fluid at reduced temperature $T^*=2.0$ ((a), at left) and $T^*=1.0$ ((b), at right). The symbols and solid lines represent the results from simulation (Shukla, 2000) and the present MFMT-cMF theory, respectively.

4. Conclusions

We have applied a density functional theory (DFT) to investigating the structures of colloids in a slit-like pore as well as the radial distribution functions of colloids represented by the hard-core Yukawa potential. The DFT is based on the combination of the modified fundamental measure theory (MFMT) for inhomogeneous hard-sphere contribution and the mean-field approximation (MF) of the Yukawa attractions. To overcome the shortcoming of the overestimation of contact density at a wall, a correction parameter *c* is introduced to the MF approximation (cMF) just as we make a correction to the energy parameter *a* in the well-known van der Waals equation of states. We found parameter $c=1+0.56\rho_{\text{b}}\sigma^3$ gives satisfactory chemical potential for the pure attractive hard-core Yukawa fluids with $\lambda=1.8$. Extensive comparisons with the GCMC simulation results for the density profiles of attractive hard-core Yukawa mixtures in a slit-like pore (pore width $H=10\sigma$) indicate that the results of the MFMT-cMF theory significantly improves the density profiles of confined colloids over that of the MFMT-MF theory, but little improvement is found for the radial distribution function of bulk colloids. For the colloids represented by attractive hard-core Yukawa potential, we observed that there is depletion at low temperature in the hard slit-like pore. Both results of the GCMC simulations and MFMT-cMF theory have confirmed that both the excluded-volume effect and the attraction between particles have significant effect on the density profiles of colloids near a hard wall.

We only make a simple correction to the MF theory using the correction parameter *c* as a linear function of reduced bulk density, and the improvement of density profiles for the colloids near a hard wall is apparent, while for the attractive wall and bulk radial distribution function, further modification to MF theory is required. The present MFMF-MF theory and its corrected form MFMT-cMF theory are simple in form, computationally efficient, and can be directly extended to multicomponent and polydisperse mixtures of colloidal particles. Therefore, the method used in this work is very promising for practical applications such as multi-component and polydisperse colloidal suspensions in confined geometry, etc.

Acknowledgement

This work is sponsored by the National Natural Science Foundation of China (Grant No. 20376037), and the National Basic Research Program of China (Grant No. 2003CB615700).

References

Boublik, T. (1970). Hard-sphere equation of state. *J. Chem. Phys.*, 53(1), 471–472.

Cochran, T. W. & Chiew, Y. C. (2004). Thermodynamic and structural properties of repulsive hard-core Yukawa fluid: Integral equation theory, perturbation theory and Monte Carlo simulations. *J. Chem. Phys.*, 121(3), 1480–1486.

Duh, D. M. & Mier-y-Teran, L. (1997). An analytical equation of state for the hard-core Yukawa fluid. *Mol. Phys.*, 90(3), 373–379.

Gonzalez-Mozuelos, P., Alejandre, J. & Medina-Noyola, M. (1991). Structure of a colloidal suspension confined in a planar slit. *J. Chem. Phys.*, 95(11), 8337–8345.

Gu, C., Gao, G. H. & Yu, Y. X. (2003). Density functional study of hydrogen adsorption at low temperatures. *J. Chem. Phys.*, 119(1), 488–495.

Henderson, D., Blum, L. & Noworyta, J. (1995). Inverse temperature expansion of some parameters arising from the solution of the mean spherical approximation integral-equation for a Yukawa fluid. *J. Chem. Phys.*, 102(12), 4973–4975.

Huang, D. M. & Chandler, D. (2002). The hydrophobic effect and the influence of solute-solvent attractions. *J. Phys. Chem. B*, 106(8), 2047–2053.

Katsov, K. & Weeks, J. D. (2001). On the mean field treatment of attractive interactions in nonuniform simple fluids. *J. Phys. Chem. B*, 105(28), 6738–6744.

Katsov, K. & Weeks, J. D. (2002). Incorporating molecular scale structure into the van der Waals theory of the liquid-vapor. *J. Phys. Chem. B*, 106(33), 8429–8436.

Lu, B. Q., Evans, R. & Telo da Gama, M. M. (1985). The form of the density profile at a liquid-gas interface dependence on the intermolecular potential. *Mol. Phys.*, 55(6), 1319–1338.

Mansoori, G. A., Carnahan, N. F., Starling, K. E. & Leland, T. W. J. (1971). Equilibrium thermodynamic properties of the mixture of hard spheres. *J. Chem. Phys.*, 54(4), 1523–1525.

Olivares-Rivas, W., Degreve, L., Henderson, D. & Quintana, J. (1997). Grand canonical Monte Carlo and modified singlet integral equations for the density profiles of a Yukawa fluid near a planar wall. *J. Chem. Phys.*, 106(19), 8160–8164.

Pizio, O., Patrykiejew, A. & Sokolowski, S. (2004). Phase behavior of ionic fluids in slit-like pores: A density functional approach for the restricted primitive model. *J. Chem. Phys.*, 121(23), 11957–11964.

Rosenfeld, Y. (1989). Free-energy model for the inhomogeneous hard-sphere fluid mixture and density-functional theory of freezing. *Phys. Rev. Lett.*, 63(9), 980–983.

Sese, L. M. & Bailey, L. E. (2003). A simulation study of the quantum hard-sphere Yukawa fluid. *J. Chem. Phys.*, 119(19), 10256–10267.

Shukla, K. P. (2000). Phase equilibria and thermodynamic properties of hard core Yukawa fluids of variable range from simulations and analytical theory. *J. Chem. Phys.*, 112(23), 10358–10367.

Tang, Y. P. (2004). First-order mean spherical approximation for inhomogeneous fluids. *J. Chem. Phys.*, 121(21), 10605–10610.

Tang, Y. P. & Wu, J. Z. (2004). Modeling inhomogeneous van der Waals fluids using an analytical direct correlation function. *Phys. Rev. E*, 70, 011201.

Vazquez, O., Herrera, J. N. & Blum, L. (2003). Static structure factor and thermodynamic properties of a binary Yukawa mixture. *Physica A*, 325, 319–332.

Velasco, E. & Tarazona, P. (1989). Wetting and drying at a solid–fluid interface. *J. Chem. Phys.*, 91(12), 7916–7924.

Wilemski, G. & Li, J. S. (2004). Nucleation near the spinodal: Limitations of mean field density functional theory. *J. Chem. Phys.*, 121(6), 7821–7828.

Yang, S. M., Miguez, H. & Ozin, G. A. (2002). Opal circuits of light — planarized microphotonic crystal chips. *Adv. Funct. Mater.*, 12, 425–431.

Yi, J. H. & Kim, S. C. (1997). Hard-sphere Yukawa fluid near a planar slit. *J. Chem. Phys.*, 107(19), 8147–8151.

You, F. Q., Yu, Y. X. & Gao, G. H. (2005). Structure of inhomogeneous attractive and repulsive hard-core Yukawa fluid: Grand canonical Monte Carlo simulation and density functional theory study. *J. Phys. Chem. B*, 109(8), 3512–3518.

Yu, Y. X. & Wu, J. Z. (2002). Structures of hard-sphere fluids from a modified fundamental-measure theory. *J. Chem. Phys.*, 117(22), 10156–10164.

Yu, Y. X. & Wu, J. Z. (2003). A modified fundamental measure theory for spherical particles in microchannels. *J. Chem. Phys.*, 119(4), 2288–2295.

Yu, Y. X., Wu, J. Z., Xin, Y. X. & Gao, G. H. (2004). Structures and correlation functions of multicomponent and polydisperse hard-sphere mixtures from a density functional theory. *J. Chem. Phys.*, 121(3), 1535–1541.

Zhang, X. R., Cao, D. P. & Wang, W. C. (2003). The effect of discrete attractive fluid-wall interaction potentials on adsorption isotherms of Lennard-Jones fluid in cylindrical pores. *J. Chem. Phys.*, 119(23), 12586–12592.

Manuscript received June 27, 2005 and accepted August 5, 2005.